

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
8 January 2004 (08.01.2004)

PCT

(10) International Publication Number  
**WO 2004/002907 A1**

(51) International Patent Classification<sup>7</sup>: **C03B 8/04**,  
37/014

(21) International Application Number:  
PCT/FI2003/000522

(22) International Filing Date: 27 June 2003 (27.06.2003)

(25) Filing Language: Finnish

(26) Publication Language: English

(30) Priority Data:  
20021269 28 June 2002 (28.06.2002) FI

(71) Applicant (for all designated States except US): **LIEKKI OY** [FI/FI]; Sorronrinne 9, FIN-08500 Lohja AS (FI).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **JANKA, Kauko** [FI/FI]; Maisterinkatu 12, FIN-33720 Tampere (FI). **RAJALA, Markku** [FI/FI]; Klaavuntie 9 A 3, FIN-00910 Helsinki (FI).

(74) Agent: **TAMPEREEN PATENTTITOIMISTO OY**; Hermiankatu 12 B, FIN-33720 Tampere (FI).

(81) Designated States (*national*): AE, AG, AL, AM, AT (utility model), AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ (utility model), CZ, DE (utility model), DE, DK (utility model), DK, DM, DZ, EC, EE (utility model), EE, ES, FI (utility model), FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK (utility model), SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

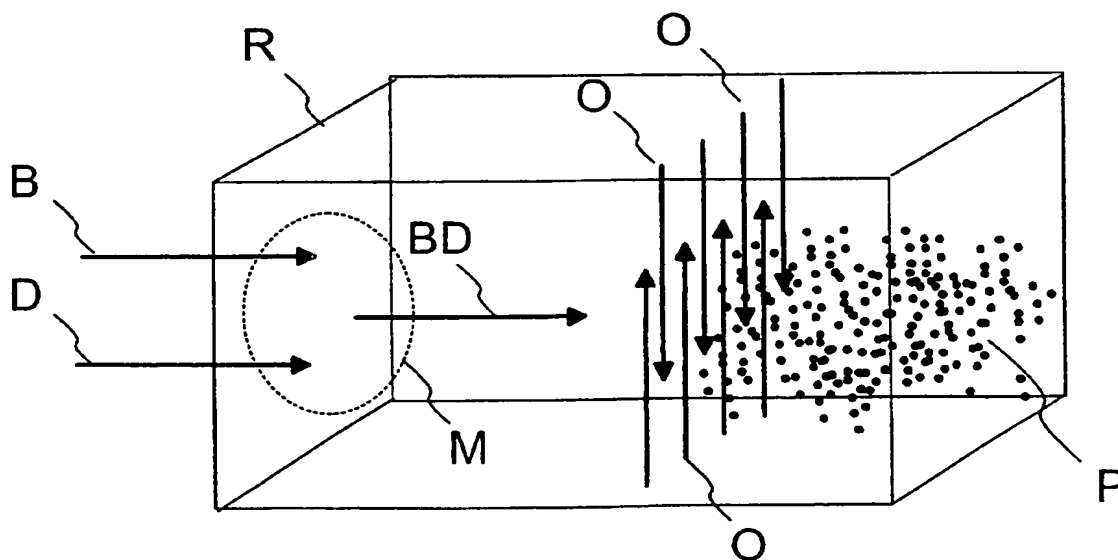
(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: A METHOD FOR THE PREPARATION OF DOPED OXIDE MATERIAL



(57) Abstract: The invention relates to a method for preparing doped oxide material, in which method substantially all the reactants (B, D) forming the oxide material are brought to a vaporous reduced form in the gas phase and after this to react with each other in order to form oxide particles (P). According to the invention, said reactants (B, D) in vaporous and reduced form are mixed together to a gas flow (BD) of reactants, which gas flow (BD) is further condensated fast in such a manner that substantially all the component parts of the reactants (B, D) reach a supersaturated state substantially simultaneously by forming oxide particles (P) in such a manner that there is no time to reach chemical phase balances.

WO 2004/002907 A1

## A METHOD FOR THE PREPARATION OF DOPED OXIDE MATERIAL

The invention relates to a method for the preparation of a doped oxide material according to the preamble of the appended claim 1.

5

An important usage of doped glass materials is light amplification waveguides, for example active optical fibres, whose light amplifying properties are based on utilizing stimulated emission. In order to make stimulated emission possible, the glass material in the core of the active optical fiber, and possibly the cladding layer surrounding the core, are doped with dopants, which are rare earth metals, for example erbium. In addition to optical fibers, the doped glass materials can also be used in different kinds of optical planar waveguides.

10 The active optical fibers are prepared by drawing glass into optical fiber from a fiber preform, which fiber preform can be created in several different ways. A generally used manner for preparing a fiber preform is to grow glass material around a mandrel, or a corresponding substrate arranged to rotate, by flame hydrolysis deposition, FHD. When the above-mentioned growing is performed from the outer periphery of the fiber preform, it is often in this connection referred to as a so-called OVD method (outer vapour deposition). The FHD method is also applied in forming glass layers required in optical planar waveguides on a planar substrate.

25

In the FHD method, a hydrogen-oxygen flame is typically used as a thermal reactor, and the glass forming base materials used in the preparation of glass material, for example silicon or germanium tetrachloride, are directed to the burner and the flame typically in a vapour form. The dopants of glass material, such as, for example, erbium, are directed to the burner and the flame typically with carrier gas as vapour or aerosol droplets, which are formed of the liquid containing dopants correspondingly either by vaporizing or by spraying.

35 Alternatively, according to the solution developed by the applicant, the dopants can be directed all the way to the burner in liquid form and be atomised as aerosol droplets, for example by using hydrogen flow, not

or chloride based sources dissolved in a liquid are used for rare earth metals, such as erbium.

5 In the growing that takes place by means of the methods described above, when silicate/alumina glass are doped with rare earth metals, one problem is the inhomogeneous distribution of dopants into aerosol particles forming glass coating. This is caused by e.g. the tendency of dopants to form pairs. In a chemical balance, erbium does not dissolve in said materials as individual ions separate from each other. In a gas  
10 phase erbium aims to oxidize into form  $\text{Er}_2\text{O}_3$  and in a solid phase erbium aims typically to a phase system  $\text{Al}_5\text{Er}_3\text{O}_{12} + \text{Al}_2\text{O}_3$  with aluminium. In other words, with aluminium erbium aims to occur clustered in its own phases. Even though the situation in a glass-like silica/alumina system is more complex than described above, the  
15 above discussion offers a good impression on how erbium acts.

Especially when using the liquid flame method, most of aluminium and a majority of erbium aims to remain in the solid residual particle, which is created from a liquid aerosol droplet when it "dries" in the flame, and  
20 wherein the abovementioned oxidation of materials into glass forming oxides takes place. Because of this, the fiber preform forming in the process typically includes at least two types of glass soot particles. Firstly, small Si-containing (or Ge-containing) particles, which are formed via condensation from vaporous base materials and the  
25 evaporation/drying following it. Secondly, aluminium and erbium containing residual particles, which are typically larger than these Si-particles. Because of these different types of particles, there is a crystallizing tendency in the glass material when it is sintered.

30 During sintering, a part of the crystals may also melt, which improves the homogeneity of the glass material. However, there is the risk that remaining dopants, especially in the larger residual particles, do not even then dissolve completely in the glass, in which case, when examined on the small scale, the consequence is that the dopants are  
35 locally inhomogeneously parted in the glass material. This weakens the light amplifying properties of the glass.

The aim of the invention is thus to make it possible to prepare doped oxide material, which is more equal in quality than before, in which oxide material the composition is on the micro level more homogeneous than before and wherein the crystal structure is as desired. The different kind of properties of oxide material become more optimal than before with the invention, in which case it is possible to manufacture better products than before from the oxide material.

10 The aim of an embodiment of the invention is to make it possible to prepare doped glass material, which is more equal in quality than before, in which glass material there is no harmful crystallization and the composition of the glass is also on the micro level more homogeneous than before. In glass material formed in this manner,  
15 there is thus less unwanted light scattering, which scattering causes attenuation/loss of light in the light guides prepared from the glass material in question. The light reinforcing properties of the glass material also become more optimal than before with the invention, in which case it is possible to manufacture better active light guides than  
20 before from the glass material, for example active optical fibers.

To attain these purposes, the method according to the invention is primarily characterized in what will be presented in the characterizing part of the independent claim 1.

25 The other dependent claims will present some preferred embodiments of the invention.

A substantial basic idea of the invention can be considered to be that  
30 all the reactants required in the preparation of doped oxide material, as well as the base materials and dopants are first brought to a vaporous form, i.e. a gas phase. Condensation of reduced components from the gas phase to a liquid phase is performed extremely fast in such a manner that all components contained in the reactants and required in  
35 forming doped material are brought substantially simultaneously to a supersaturated state, in which case the composition of liquid droplets forming in this manner and solid particles forming immediately from

producing other doped oxide materials by possibly implementing minor changes in the embodiment according to the example. The invention will be described with reference to the appended figures, in which

- 5     Fig. 1        shows, in principle, a structure of a reactor according to the invention in a perspective view,
- Fig. 2        shows, in a principle view, a cross section of the reactor according to the invention, and
- 10     Fig. 3        shows, in a principled side-view, another reactor according to the invention.

15     All the reactants required in the preparation of doped glass material according to the invention, as well as the base materials (for example Si or Ge) and dopants (for example Al and rare earth metals) are in the beginning brought to a vaporous form i.e. the gas phase, by appropriately increasing the temperature of said materials and by choosing an appropriate chemical composition for each reactant.

20     Heating the reactants can be implemented with any manner apparent as such to a man skilled in the art. For example, silicon tetrachloride  $\text{SiCl}_4$  can be used as the base material of glass material and aluminium and erbium as the dopant, the latter either as nitrates or chlorides. The compounds used as the sources of aluminium and erbium can be,

25     for example, dissolved in appropriate liquids and evaporated further to a gas phase by heating the solutions in question. In conveying the reactants brought to the gas phase, it is possible to utilize appropriate carrier gases.

30     The base materials and dopants in a gaseous or reduced form are next guided mixed together or still as separate gas flows B, D to the reactor R functioning as a flow channel by at the same time retaining their temperature such that the base materials and dopants B, D remain in a vaporous form. The ratio between the base materials and dopants can

35     be adjusted by changing the ratio of the gas flows B, D, for example, by means of adjustable valves, such as mass flow controllers, or some other appropriate manner.

It is clear to a man skilled in the art that because the material is a glass-like material, which has no clear melting or solidification temperature, the term "condensation" should here be understood widely. In other words, depending on the situation, either a liquid or  
5 solid glass particle can be understood to form as a result of condensation.

In order to understand the embodiment of the invention described above, it is important to note that the saturated vapour pressure of the  
10 oxidized forms of the reactants, in a certain temperature being examined, is significantly lower than in connection with corresponding reduced forms. Because of this, the fast condensation of the reactants in the gas phase can be performed by mixing fast oxidative gases to the gas flow of the reduced reactants.

15 According to the advantageous embodiment of the invention presented in Fig. 1, the condensation/oxidation is performed by conducting intensive jets O of oxidative gases to the reactor, which jets are advantageously located transverse to the gas flow BD of the reactants.  
20 Preferably, jets O of oxidative gases are further located on the two opposite walls of the reactor according to Fig. 2 in such a manner that the gas jets O, which are opposite and adjacent in the cross-direction of the reactor, are located overlapping each other. This intensifies the turbulence created by the jets O of oxidative gases to the gas flow BD  
25 of the reactants, which turbulence mixes the oxidative gases O and the reactant gases BD effectively together. Jets O of oxidative gases can also be arranged onto more walls of the reactor R, or they can be directed in some other manner promoting turbulence and mixing in relation to the gas flow B, D of reactants.

30 For example, oxygen or carbon dioxide can be used as oxidative gases. Oxidative gases O can, when entering the reactor, be in the same temperature as the reactant gases in their reduced form, in other words hot. Thus, the condensation is mainly caused by the change in  
35 the vapour tension experienced by the reactants when they oxidize to oxides. Advantageously the oxidative gases are, however, "cold", which intensifies and accelerates the condensation.

The structure of the reactor R, LR can be oven-like in such a manner that the walls of the reactor are heated. Advantageously, materials resistant to high temperatures, such as quartz, are used as the material  
5 of the reactor. The walls of the reactor can be partly or entirely porous, in which case, for example, different kinds of shielding gases can be directed through the walls inside the reactor. The shape of the cross section of the flow channel formed by the reactor R, LR can be a rectangle, circle, or some other shape appropriate for the purpose.

10

When forming doped glass materials, it is also possible to use chlorine-free reactants, such as TEOS (tetraethylortosilicate) or GEOS (tetraethoxygermanium) in an appropriate form as base materials B. In addition to the ones mentioned above, it is possible to use also other  
15 rare earth metals and lantanides as dopants D, such as, for example, neodymium, and further also phosphorus, borium and/or fluorine.

The glass particles formed by using the method according to the invention can be collected according to prior art onto an appropriate  
20 substrate, for example, around a rotating mandrel or on a planar substrate, on which surface is thus formed a porous glass layer, which can in later stages of process be sintered into a compact glass layer. The glass particles can, however, also be collected by other means, for example as dusty powder, which can later be used as desired in  
25 preparing glass components.

It is, of course, obvious for anyone skilled in the art that by combining the modes of operation presented above in different ways in connection with different embodiments of the invention, it is possible to  
30 provide various embodiments of the invention in accordance with the spirit of the invention. Therefore, the above-presented examples must not be interpreted as restrictive to the invention, but the embodiments of the invention can be freely varied within the scope of the inventive features presented in the claims hereinbelow.

35

In the drawings, only the parts and components important for understanding the principle of the invention are presented, and it is

Claims:

1. A method for the preparation of doped oxide material, in which method substantially all the reactants (B, D) forming the oxide material are brought into a vaporous reduced form in the gas phase and after this to react with each other in order to form oxide particles (P), **characterized** in that said reactants (B, D) in vaporous and reduced form are mixed together as a gas flow (BD) of the reactants, which gas flow (BD) is further condensed fast in such a manner that substantially all the components of the reactants (B, D) reach a supersaturated state in said gas flow substantially simultaneously by forming oxide particles (P) in such a manner that there is no time to reach a chemical phase equilibrium.
2. The method according to claim 1, **characterized** in that said oxide material is doped glass material, which is formed of the base materials (B) and dopants (D) of glass material by bringing these to react with each other in the gas phase in a vaporous reduced form and to condensate further into glass particles (P).
3. The method according to claim 1, **characterized** in that the fast condensation of reactants (B, D) into oxide particles (P) is achieved by fast oxidation of reactants (B, D).
4. The method according to claim 3, **characterized** in that said fast oxidation and condensation of reactants (B, D) is achieved by directing one or more jets (O) of oxidative gases to the gas flow (BD) of the reactants, preferably jets formed of oxygen and/or carbon dioxide.
5. The method according to claim 4, **characterized** in that said one or more jets (O) of oxidative gases are directed to the gas flow (BD) in a manner causing strong turbulence and mixing.
6. The method according to claim 4, **characterized** in that the formation of oxide particles (P) is intensified by directing said one or more jets (O) of oxidative gases to the gas flow (BD) of reactants as colder than said gas flow.



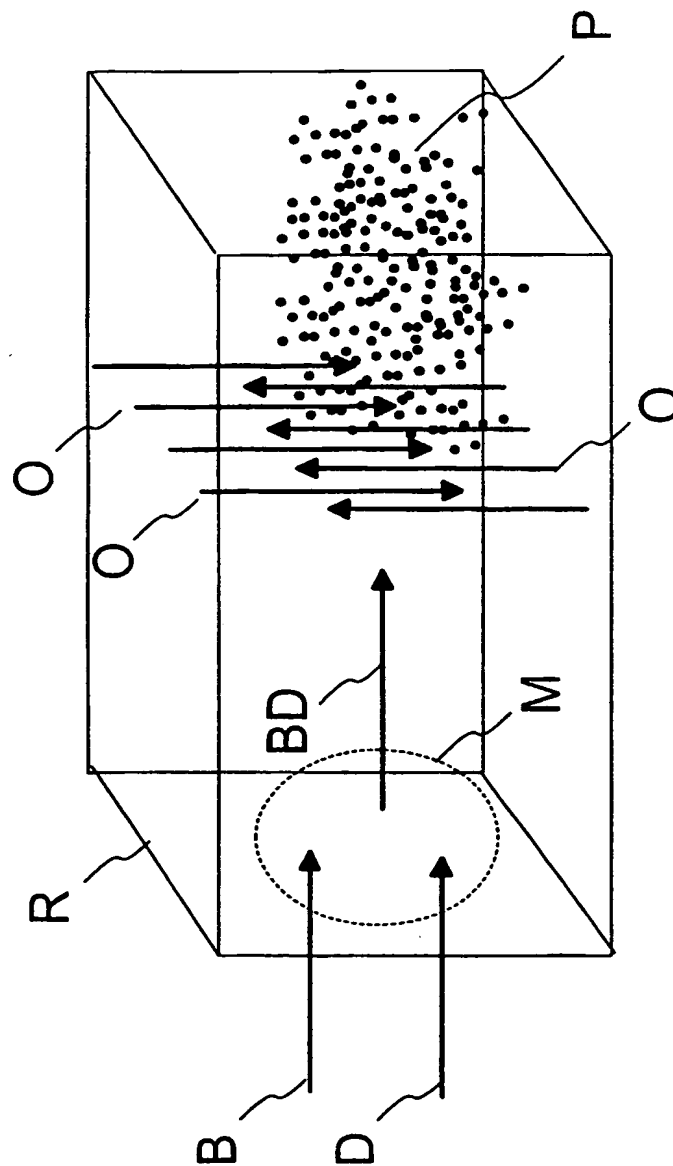


Fig. 1

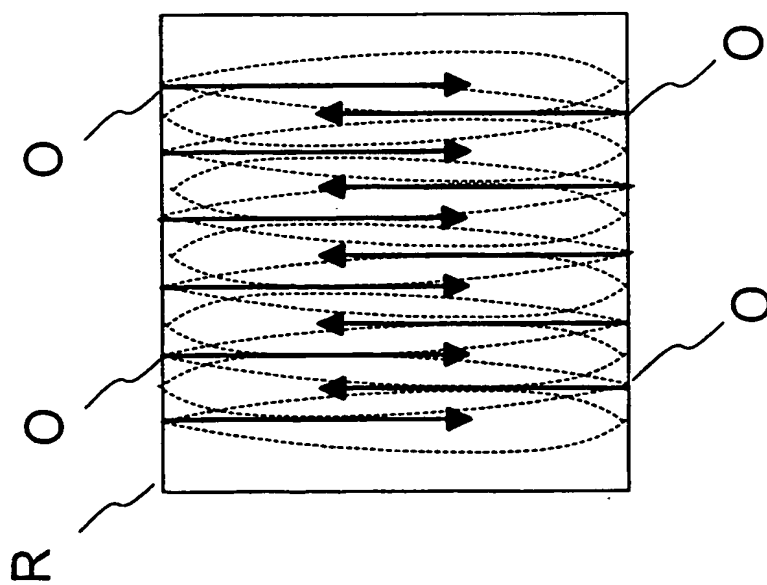


Fig. 2

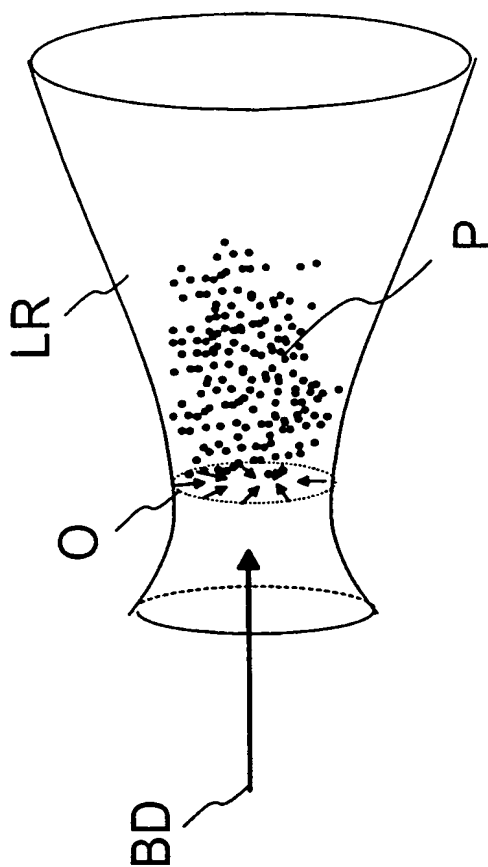


Fig. 3

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/03/00522

## A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C03B 8/04, C03B 37/014

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C03B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-INTERNAL

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2002/0005051 A1 (JOHN T. BROWN ET AL), 17 January 2002 (17.01.02), figure 19, paragraph (0066), (0063), (0064)  --	1-10
A	US 4278458 A (PAUL B. O'CONNOR ET AL), 14 July 1981 (14.07.81), column 1, line 41 - line 47; column 2, line 15 - line 22; column 2, line 34 - line 38, column 2, line 62 - line 66  --	

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

\* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

Date of the actual completion of the international search

19 Sept 2003

Date of mailing of the international search report

19-09-2003

Name and mailing address of the ISA/  
Swedish Patent Office  
Box 5055, S-102 42 STOCKHOLM  
Facsimile No. +46 8 666 02 86

Authorized officer

Linda Melin/MP  
Telephone No. +46 8 782 25 00

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

26/07/03

International application No.

PCT/JP 03/00522

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2002/0005051 A1	17/01/02	NONE	
US 4278458 A	14/07/81	NONE	